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Modelling and experimental investigations of thin films of Mg phosphorus-doped tungsten bronzes obtained by ultrasonic spray pyrolysis

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Summary

In this study, the synthesis of thin films of Mg phosphorus doped tungsten bronzes (MgPTB; $MgHPW_{12}O_{40}{\cdot}29H_2O$) by the self-assembly of nano-structured particles of MgPTB obtained using the ultrasonic spray pyrolysis method was investigated. As the precursor, MgPTB, prepared by the ionic exchange method, was used. Nano-structured particles of MgPTB were obtained using the ultrasonic spray pyrolysis method. The nano-structure of the particles used as the building blocks in the MgPTB thin film were investigated experimentally and theoretically, applying the model given in this article. The obtained data for the mean particle size and their size distribution show a high degree of agreement. These previously tailored particles used for the preparation of thin films during the next synthesis step, by their self-assembly over slow deposition on a silica glass substrate, show how it is possible to create thin MgPTB films under advance projected conditions of the applied physical fields with a fully determined nanostructure of their building block particles, with a relatively small roughness and unique physical properties.

Introduction

Heteropoly compounds (HPCs), such as magnesium phosphorus doped tungsten bronzes (MgPTB), can be applied in specific composite membranes. Organic–inorganic composite membranes with different inorganic heteropoly acids (HPAs) as additives maintain good proton conductivity at atmospheric pressure and elevated temperatures, over 100°C, in fuel cells (Dimitrijević *et al.*, 1993; Mioč *et al.*, 1994, 1995, 2005). The chemical resistance, thermal stability and conductivity of Mg–PTB suggest the possibility of such an application. However, membranes and membrane electrodes assembled with HPCs, both the free acids and their salts, have several restrictions: high solubility in aqueous media and high dependence of proton conductivity on the degree of hydration. To overcome these disadvantages, it is necessary to develop solid-state electrolytes with high stability and a satisfactory high conductivity. Such compounds could be salts of large cations, such as Cs^+, Rb^+, K^+ and NH_4^+, insoluble salts or different forms of metal-doped PTB, such as MgPTB (Dimitrijević *et al.*, 1993; Mioč *et al.*, 1994).

This article focuses on PTB doped with magnesium ions, obtained from Keggin's anion structures. The method of calcination of Mg–WPA salt was used to obtain the Mg–PTB (Mioč *et al.*, 1995).

In previous investigations, a combination of thermal and ionic exchange methods was used to obtain Me-PTB powders. Generally, this is an exothermic method of solid–solid re-crystalization and a collapse of the Keggin's anion by the ionic exchange of previously treated 12-tungstophosphoric acid (WPA) as the precursor (Mioč *et al.*, 2005). Metal-doped bronzes (M_x–PTB, M_x–metal) can be produced in a very wide range of compositions because about 50 elements of the Periodic Table of the elements could be incorporated in HPCs as hetero or addenda atoms.

In this study, special attention was directed to ultrasonic spray pyrolysis, as one of the most promising new methods for the production of MgPTB. In previous investigations, it was shown that this method is very useful for the synthesis of a variety of ceramic powders (Al_2O_3, mullite, cordierite, SiO_2, SiO_2, rare earth dopants, calcium hydroxyapatite, TiO_2, AgI, Gd_2SiO_5, Y_2SiO_5, Gd_4CaSiO_{13}, HPTB bronzes) with previously defined chemical and phase compositions (Jokanović *et al.*, 1996; Jokanović, 2005).

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During particle formation by the ultrasonic spray pyrolysis process, many parameters affect the particle morphology and mechanism of their formation. The most significant among them are the frequency of the ultrasonic waves, the temperature gradient between the surface and the centre of the droplet obtained by ultrasonic excitation, the viscoelastic properties of the droplet and their level of rigidity, the behaviour of a droplet during its collision with other droplets, the thermodiffusion coefficient inside the droplet, the permeability of the shell formed on the droplet surface during its solidification and the physico-chemical properties of the precursor.

It seems as if the frequency of atomization and the concentration of the precursor are the dominant factors influencing the mean particle size and distribution and morphology (Jayanthi *et al.*, 1993; Jokanović *et al.*, 1996, 2004; Jokanović, 2005; Lenggoro *et al.*, 2000; Esleman *et al.*, 2006).

Since then, there have been many attempts to explain the mechanism of atomization of an aerosol droplet under the influence of ultrasonic excitation. Among others (Jayanthi *et al.*, 1993; Lenggoro *et al.*, 2000; Esleman *et al.*, 2006), the model of capillary waves developed by V. Jokanovic *et al.*, which was applied in this study in investigations of MgPTB, is a very interesting new approach, which explains the mechanism of formation of aerosol droplets by invoking the break-up mechanism of capillary waves formed on the meniscus surface of a precursor liquid (Jokanović *et al.*, 1996, 2004; Jokanović, 2005).

It is shown that the theoretical data predicted by the model and the experimental data obtained by measurements of the diameters of the formed MgPTB particles are in fair agreement, showing in such a way that the model can be successfully applied to this system.

That resulted in the idea that not only can the mean particle size and distribution be predicted but the model could also be employed to determine the precursor concentration and other atomization conditions required to produce exactly the required particles followed by the subsequent step of their very slow precipitation on a substrate surface, thus obtaining thin films that are completely composed of such in-advance created particles (Jokanović *et al.*, 1996, 2004; Jokanović, 2005).

Experimental

The MPTB was prepared in two steps, that is the synthesis of $H_3PW_{12}O_{40}{\cdot}29H_2O$ and the ion exchange of H^+ in the heteropoly acid with Mg^{2+} ions. $NaWO_4$ was used as the precursor of W and H_3PO_4 as the precursor for P (H_3PO_4 was mixed with HCl). Diethyl ether and distilled water are also added. The heteropoly acid $H_3PW_{12}O_{40}{\cdot}29H_2O$ was extracted into the denser phase of water saturated with diethyl ether. $MgHPW_{12}O_{40}{\cdot}nH_2O$ (MgHPW) was obtained by the ion exchange at 80°C of the H^+ ions in the heteropoly acid with Mg^{2+} ions using $MgCl_2$. MgHPW diluted in distilled water was used as the precursor for MgPTB in the following step of ultrasonic spray pyrolysis. Finally, the solution was pyrolyzed under the following conditions: the frequency of the ultrasonic atomizer was 1.7 MHz, the working temperature in the tabular furnace was 1000°C and the air carrier gas flow rate was 0.011 ms^{-1}. The obtained particles were then very slowly self-assembled on the surface of silica substrates.

The morphology, size distribution, the mean size of MgPTB particles and their sub-structure were determined by scanning electron microscopy, SEM (JOEL: JKSM-5300; JEOL Ltd., Tokyo, Japan). The structures of the obtained self-assembled thin films were investigated by AFM (USPM, Quesant Instrument Co., Institute of Nuclear Sciences Vinca, Belgrade, Serbia). The thickness of the film was determined using an ALFA STEP 500 Surface Profiler (Tencor Instruments, Mountain View, CA, USA).

The synthesized powders were analyzed by X-ray diffractometry, XRD diffractometer (Philips PW 1050; Philips, Almelo, the Netherlands) in Bragg-Bretano geometry, with vertical goniometer and computer controlled step scanner, with a generator current of 35 mA at 40 kV, using Cu-K$\alpha_{1,2}$-Ni–filtered radiation. The diffraction pattern was recorded in the 2θ range from 10° to 65°, with a scanning step of 0.02° and a time interval of 4 s per step. Data were processed and presented using computer graphics (Traces V 4.0) and a comprehensive CD-ROM database (JCPDS).

Theoretical design

A theoretical model of the genesis of an aerosol droplet, as the main part of the process of forming MgPTB particles, was developed using a three-dimensional model of the spheroid waves formed in the system (liquid column, created by the geometrical form of the vessel filled with a given solution) by the forced field of an ultrasonic oscillator. The forced frequency of the ultrasonic oscillator causes the formation of equivalent oscillations inside the liquid and induces the formation of transversal and longitudinal disturbances. By superposition of these deformations, complex three-dimensional waves are formed. In general, for a liquid column with a significant liquid depth, owing to different damping factors of transversal and longitudinal oscillations, produced waves on the surfaces of liquid column, the meniscus, are ellipsoidal shape. Therefore, degeneration of the forced frequency of the ultrasonic oscillator occurs. This affects the appearance of the oscillation spectrum, and as a consequence, results in the generation of a complete spectrum of droplet-size distribution. This spectrum, in agreement with the Jokanovic *et al.* model, can be explained by the following expression (Jokanović *et al.*, 1996, 2004; Jokanović, 2005):

$$d_{\mathrm{d}} = \frac{1}{\pi}\left\{\left[\frac{2\pi\sigma}{\rho f^2}\right][l\,(l-1)\,(l+2)]\right\}^{1/3}, \qquad (1)$$

where l is an integer number, which depends on the eccentricity of the capillary waves, σ is the surface tension of the liquid, ρ the precursor density, f is the frequency of the capillary waves and d_d is the droplet diameter.

To obtain the diameters of particles formed from an aerosol droplet through the solidification process, the following equation is used (Jayanthi *et al.*, 1993):

$$d_p = d_d \left(\frac{c_{pr} M_p}{\rho_{pr} M_{pr}} \right)^{1/3}, \quad (2)$$

where d_p is diameter of the powder particle, ρ_p the powder density, M_p the molecular mass of the powder, c_{pr} the precursor concentration of the sprayed solution and M_{pr} the molecular mass of precursor.

Results and discussion

The MgPTB particles were highly spherical in shape as can be seen in Fig. 1. During previous investigations, it was noticed that the time t_{eq} for a particle diameter at which the temperature in the bulk of the droplets becomes equal to the surface temperature is a very important parameter that determines the mechanism of particle formation and its morphology. If this time is short enough, a uniform supersaturation of the solution in the bulk of the droplet occurs (Jayanthi *et al.*, 1993; Jokanović *et al.*, 2004; Jokanović, 2005). This results in their volume precipitation and full density of the powder inside its volume. This is fulfilled for smaller particles, whereas larger particles can have an empty space in the centre, as can be seen for some particles in Fig. 1. It is evident that the prevailing mechanism of MgPTB precipitation is volume precipitation, even for particles with the mean size diameter. The largest particles only precipitated partially by the surface precipitation mechanism (Jokanović *et al.*, 1996, 2004; Jokanović, 2005).

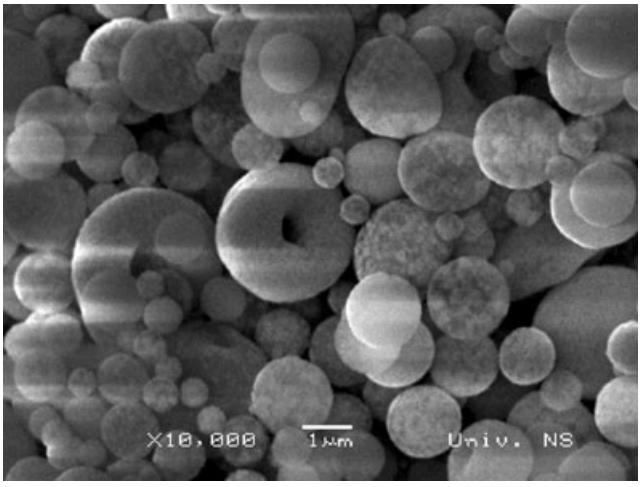

Fig. 1. Typical distribution of particle size diameters of MgPTB particles.

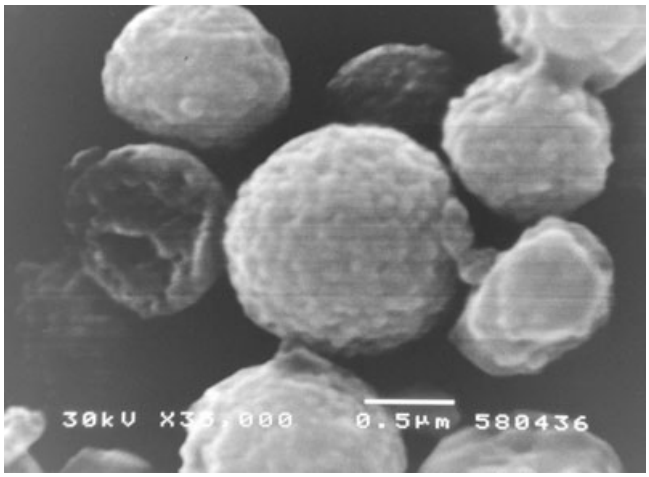

Fig. 2. Typical sub-structure of MgPTB particles.

Therefore, some of the largest particles were hollow, as can be seen in Fig. 1. Such particles have an empty space in the centre surrounded by a full density ring, the depth of which is dependent on the precursor concentration.

For an adequate estimation of the particle morphology and size distribution, which includes the full spectra of discrete diameters and the frequency of appearance, all the data obtained from the SEM images were treated using the required statistical fitting data functions, that is Gaussian, Lorentzian and Voight functions.

By measurement of the diameters of around 200 MPTB particles, the mean diameter of the particles and their size

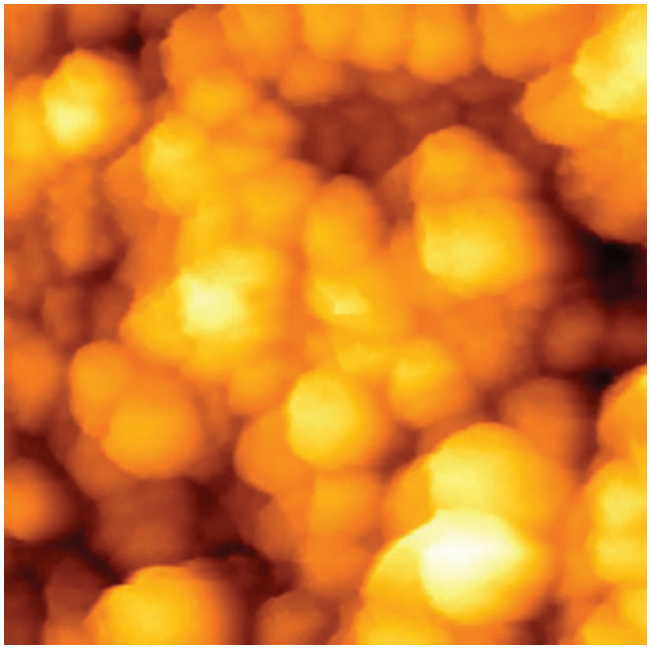

Fig. 3. Appearance of thin film obtained from self-assembled MgPTB particles.

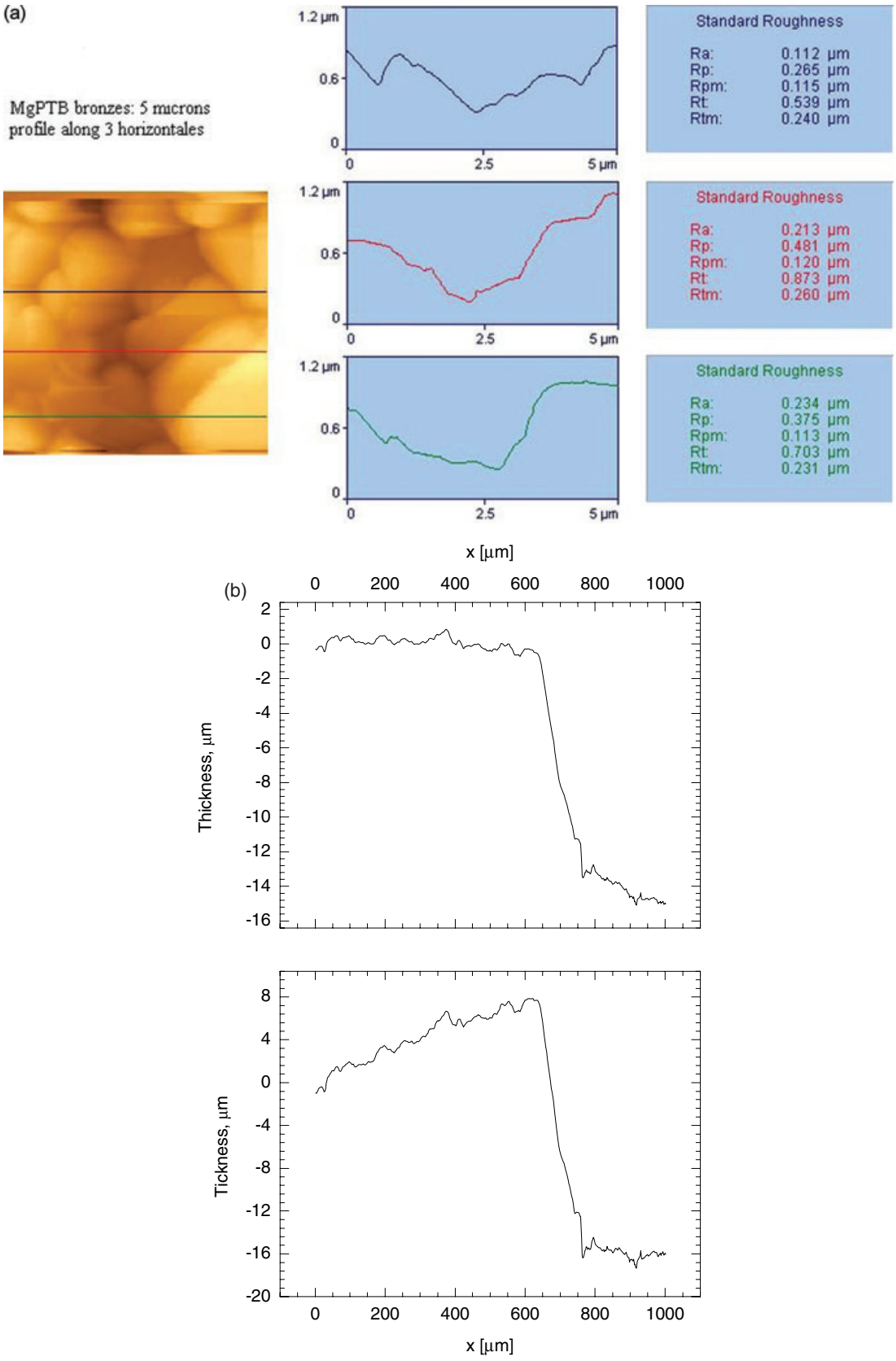

Fig. 4. Roughness of MgPTB thin film (a-AFM) and thickness (b-ALFA STEP 500 Profiler).

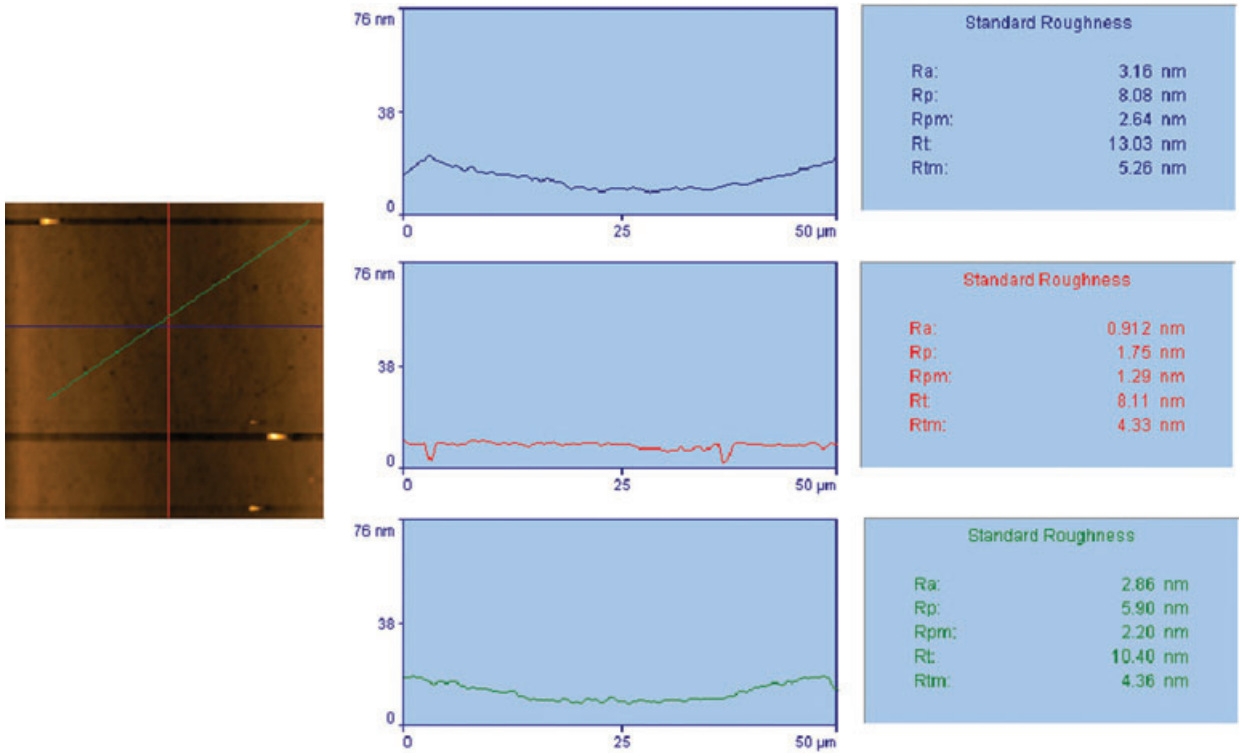

Fig. 5. Glass substrate roughness.

distribution were determined. From these data, the mean diameter of the particles was found to be 1.33 μm, whereas the size range was 0.4–2.3 μm. Most of the particles belonged to the size range 0.6–2.1 μm (about 85% of the particles). The obtained results for the mean particle size were almost identical (1.38 μm), irrespective of the applied fitting data function (Gaussian, Lorentzian or Voight) – in all cases that is.

Inside of the particles, as can be seen in Fig. 2, at the lower level (the level of sub-particles), sub-particle structure

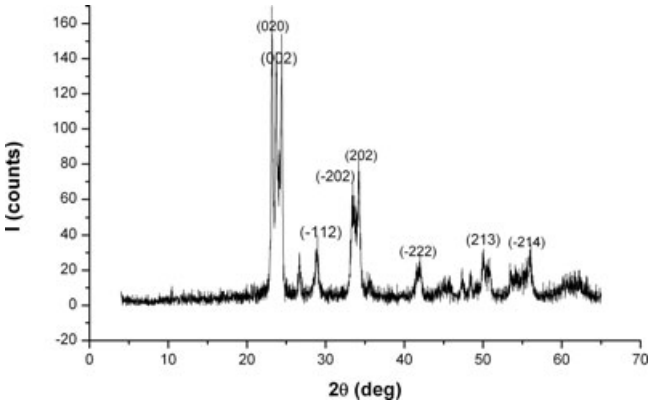

Fig. 6. XRD spectra of MgPTB particles.

design was noticed in agreement with the model of sub-particle design. Their mean diameter calculated from the experimental data was 55 nm. By the model of the sub-particle design, the theoretically estimated value was very similar (51 nm) (see corresponding equation in references Jayanthi *et al.*, 1993; Jokanović *et al.*, 1996; Jokanović, 2005).

The values of the mean diameter of the particles (1.35 μm) and the size distribution were also estimated using Eqs 1 and 2 of the theoretical model of the break-up of capillary waves (Jokanović *et al.*, 1996, 2004; Jokanović, 2005).

It is clear by comparison with the experimental data (mean diameter 1.33 μm and size distribution 0.6–2.1μm) that they were both in good mutual agreement.

The self-assembled thin films, by contrast, exhibit a structure completely determined by shape and diameter of the self-assembled nano-structured particles (Fig. 3). They are characterized by a very low roughness (an average roughness of 10 nm, significantly less than 0.5 μm), which is close to the differences in the particle diameters of the various powder particles (Fig. 4). For comparison, the roughness of the glass substrate was investigated (Fig. 5). Its average roughness was 5 nm, and hence it obviously cannot have any influence on the roughness of the final film.

The thickness of the MgPTB film was investigated using the ALFA STEP 500 Surface Profiler method. The jump of the needle of the Surface Profiler between the uncovered part of

the substrate (zero point) and the coated surface defines the film thickness. By corresponding measurements, it is found that the average thickness of this film was about 20 μm (Fig. 4). The film consisted of rows of particles (Fig. 5) arranged regularly one after another from the bottom to the top of the film. Therefore, despite its significant thickness, the roughness of the film was relatively small because the film deposition process was very slow (row by row).

This fact demonstrates that it really is possible to create, in the first step, particles that have a distribution and structure at the sub-micro level and sub-structure at the nano level pre-determined by the theoretical model, which can then be deposited as a corresponding thin film on the surface of a substrate. The main consequence of so-created films is that their physical characteristics are completely the same as those of the particles from which they were designed. These films can be designed from particles, with more or less developed surface area and activity, in agreement with their sub-design.

Phase composition

The XRD pattern of the MgPTB powder is given in Fig. 6, from which it is clear that the obtained MgPT bronze crystal form was monoclinic because all the characteristic planes of these bronzes are present as follows: (020)-I_{100}, (002)-I_{89}, (−202)-I_{54}, (202)-I_{41}, (213)-I_{24}, (−222)-I_{17} and (−112)-I_{16} (Fig. 5).

Conclusion

In this paper, the synthesis of thin films by the self-assembly of previously tailored, nanostructured MgPTB particles by ultrasonic spray pyrolysis is described. These films were self-assembled using previously obtained nano-particles as the building blocks with specific arrangements of these elements.

The experimental data obtained by statistical treatment of the measured data of particle size and distribution by SEM (mean diameter 1.33 μm and size distribution 0.6–2.1μm) and the data obtained by application of the model of break-up of capillary waves (mean diameter 1.35 μm and size distribution (1.1–2.4 μm) were in mutual satisfactory agreement. The mean experimental sub-particle diameter (55 nm) and that estimated by the theoretical model (51 nm) are also in very good agreement. The average film roughness, measured by AFM, was significantly below 0.5 μm, whereas the mean film thickness, measured by an ALFA STEP Surface Profiler, was about 20 μm.

All these facts confirm the full applicability of the examined theoretical model of break-up of capillary waves for the prediction not only of nano-structural design of MgPTB particles but also of the corresponding thin films produced by their self-assembling.

Acknowledgement

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